Experimental Tests of the Global Nature of the Staebler-Wronski Effect in Amorphous Silicon

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ABSTRACT

The results of experimental studies designed to determine if the Staebler-Wronski effect involves changes in the long-ranged disorder in a-Si:H are reported. We have measured the difference in activation energy from measurements of the dark conductivity and thermoelectric power for a series of a-Si:H films synthesized under a wide range of deposition conditions. This activation energy difference has been interpreted as reflecting the long-ranged disorder induced by compositional modulations or potential fluctuations. We have found absolutely no change in this activation energy difference due to the Staebler-Wronski effect. Measurements of the non-Gaussian statistics which characterize the conductance fluctuations (1/f noise) are also found to remain unchanged after light exposure.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has long been considered one of the most promising materials for large area, low cost photovoltaic applications. A major problem preventing a-Si:H from fulfilling its technological promise is the Staebler-Wronski effect (SWE), a light-induced increase in defect density accompanied by a decrease of the semiconductor's conductance. Solar cells fabricated using a-Si:H can typically lose nearly 5% of their initial conversion efficiency due to this effect. Consequently, since its discovery in 1977 [1] there has been considerable effort applied towards ascertaining the microscopic origin of this light-induced defect creation. While a great deal of progress has been made, basic issues, such as whether the photogenerated defects result only from local bond breaking or whether there are long-ranged atomic rearrangements associated with defect creation, remain unanswered.

Long-ranged disorder at the mobility edge, caused by structural inhomogeneities in the composition of a-Si:H and potential fluctuations caused by charged defects, will result in long-ranged fluctuations of the energy of the mobility edge on length scales of 10^2 to 10^3 Å (much longer than the inelastic scattering length of ~ 5 Å). This disorder is believed to be responsible for the difference in the value of the activation energy as measured by the dark conductivity (E_σ) when compared to the same quantity measured by the thermoelectric power, or thermopower (E_S) [2]. E_σ and E_S can differ by as much as 100 to 300 meV for a-Si:H. In a-Si:H the magnitude of E_Q (E_σ - E_S) is a measure of the magnitude of the long-ranged disorder. Thus we would expect to see E_Q increase as the electronic quality of a sample degrades (as reflected in lower dark conductivity and higher dangling bond defect density). An increase in E_Q following light exposure would indicate a shift in the conduction band to higher energies.

Previous noise measurements on a-Si:H films have found that the coplanar current fluctuations have a spectral density which is well described by a 1/f frequency dependence for frequencies f ranging from $1 < f < 1000$ Hz. Moreover, analysis of the non-Gaussian statistics which characterize the 1/f noise indicates the existence of cooperative interactions between the fluctuators. Increasing the structural disorder of the a-Si:H film by varying the deposition conditions [3,4] decreases the correlations of the noise power, consistent with the suggestion that the non-Gaussian 1/f noise is sensitive to the long-ranged disorder.

2. Experimental Techniques

We have measured both the dark conductivity and the thermopower of a number of n-type samples of a-Si:H (doped with phosphorus) as a function of temperature before and after illumination. We have also examined the conductance noise of a film deposited at 150 °C. The samples were all deposited at the University of Minnesota in a capacitively coupled RF (13.56 MHz) system using plasma-enhanced chemical vapor deposition of silane (SiH_4) and phosphine (PH_3) for n-type doping. Prior to any measurements, a sample is annealed at 180 °C for at least one hour and then cooled to 50 °C. The state of the sample before any illumination is referred to as State A. Following light soaking the film is denoted as being in State B and can be returned to State A by a high temperature (~150 °C) anneal. Light soaking is performed with ~ 100 mW/cm^2 of heat-filtered white light from a tungsten-halogen lamp.

3. Results

All the samples studied here were measured both in State A and State B (following a light exposure of ~ 24 hours). We first examined a series of films grown at different deposition temperatures (ranging from 80 to 250 °C), with the RF power of 3 W and the doping ratio of $[PH_3]/[SiH_4] = 4 \times 10^{-4}$ kept constant. Figure 1 plots the change in the dark conductivity activation energy following light exposure (ΔE_σ) along with ΔE_Q for this series of samples against the film's value of E_Q in State A. Here ΔE is defined as the activation energy difference between its value in State B and in State A. All four of these samples exhibit a clear shift in E_σ (and E_S), but no significant shift in E_Q. Figure 1 also shows the values of ΔE_σ and ΔE_Q for two additional samples: (1) A film deposited at a RF power of 1

W with the same doping level as the temperature deposition series and (2) a film with a doping level of $[PH_3]/[SiH_4]$ = 4 x 10^{-3} deposited at a RF power of 3 W (both deposited at 250 °C). No change in E_Q is observed for either of these samples while both experienced a change in both E_σ and E_S. Thus neither altering the deposition power nor increasing the ratio of the phosphorus to silicon by a factor of 10 leads to any significant shift in E_Q.

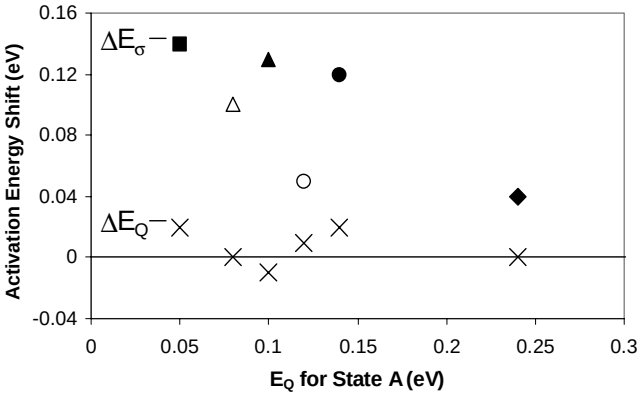

Figure 1: Plot of the shift in activation energy for the conductivity and Q-function with respect to E_Q in State A. The solid symbols are the values of ΔE_σ for the films in the temperature deposition series (solid symbols) described in the text. The square, triangle, circle and diamond represent the 250, 150, 100, 80 °C films respectively. The open triangle is for the film deposited at 1 W with a doping of 4 x 10^{-4} and the open circle is for the film deposited at 3 W with a doping of 4 x 10^{-3} (both deposited at 250 °C).

All of the films studied here were examined in a State B produced by ~ 24 hours of light exposure. It is possible that this period of illumination may not be long enough to produce a detectable shift in E_Q. We have measured a film deposited at 250 °C at a RF power of 3 W with a doping ratio of 4 x 10^{-4} after light exposures of ~ 100 hours and ~ 340 hours. No noticeable shift in E_Q is observed even after light exposures of this magnitude.

The first and second noise power spectra for the film deposited at 150 °C is shown in Figure 2 for States A and B. The second spectra was obtained from a series of 1024 FFTs of the noise power for the 320-640 Hz octave taken over time. Figure 2a displays the clear 1/f dependence of the first spectra noise power in both states; no significant change in the noise power is observed after light exposure (the applied voltage is adjusted so that identical currents flow through the film in each state). The second spectra (Fig. 2b) also displays approximate 1/f behavior, and again no consistent change is seen following light exposure. The non-zero slope of the second spectra reflects the non-Gaussian nature of the noise (the second spectra of a Gaussian noise source would be frequency independent).

4. Conclusion

Despite previous reports of a shift in E_Q in n-type films [5,6] we do not find here any such change. These results

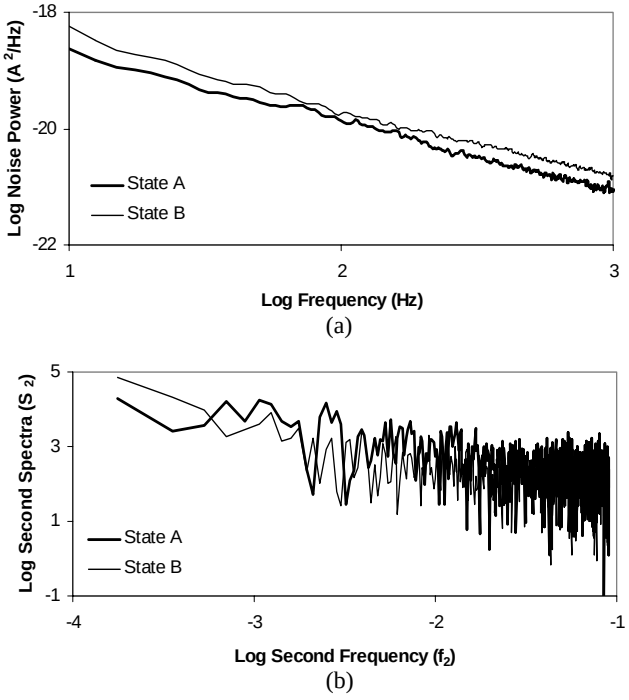

Figure 2: Plot of the first spectra (a) and second spectra (b) for the film deposited at 150 °C with doping of 4 x10^{-4}.

suggest that the Staebler-Wronski effect does not involve any changes in the long-ranged disorder of the mobility edge. The lack of observed change in the non-Gaussian noise behavior following light exposure supports this conclusion. The changes in the conductivity and thermopower activation energies are consistent with a statistical shift of the Fermi energy deeper into the band gap, induced by the creation of new dangling bond defect states from the recombination of photo-excited electron-hole pairs. These experimental studies thus indicate that the Staebler-Wronski effect can be associated with purely local bond breaking events, and that efforts to eliminate or modify the long-ranged disorder in an attempt to remove the Staebler-Wronski effect will be ineffectual.

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REFERENCES

[1] D. L. Staebler and C.R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[2] R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, 1991).
[3] D. Quicker and J. Kakalios, *Phys. Rev. B*, **60**, 2449 (1999).
[4] P. W. West, D. Quicker, H. M. Dyalsingh and J. Kakalios, Materials Research Society Symposia Proceedings (Materials Research Society, Pittsburgh, PA), **467**, 215 (1997).
[5] D. Hauschildt, W. Fuhs and H. Mell, Phys. Stat. Sol. (B) **111**, 171 (1982).
[6] P. Agarwal and S. C. Agarwal, Diffus. Defect Data B, Solid State Phenom. **55**, 140 (1997).